HYDROGEN BONDING IN ALCOHOLS

Thesis by

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Summary

It is usually assumed in optical absorption work that the natural stretching frequency of the hydroxyl group in an alcohol is appreciably changed by hydrogen bonding. A survey of work relating to hydrogen bonding in alcohols favors this assumption. Moreover, it appears that the deviation of alcohols in solvents such as carbon tetrachloride from Henry's law is primarily due to hydrogen bonding polymerization, the extent of such deviation being the same for the lower aliphatic alcohols and phenol.

Optical transmission measurements on dilute solutions of methyl alcohol and of ethyl alcohol in carbon tetrachloride were used to determine for these alcohols the dimerization constants associated with the reaction

$$2\ ROH \rightarrow (ROH)_2$$

These constants in turn were used in support of the contention that the polymerization constants associated with the reactions

$$(ROH)_{g-1} + ROH \rightarrow (ROH)_g$$

are not independent of g as has been assumed on occasion.

The viscosity of solutions of alcohols in carbon tetrachloride is briefly discussed in a semi-quantitative manner.

I. Introduction:

The anomalous physical properties associated with substances containing hydroxyl and similar groups have as a result of the extensive investigations of the properties of the hydrogen bond been re-expressed in terms of chemical association, albeit a weak variety. The re-expression has not been quantitative in all cases but it has at least systematized several classes of physical phenomena: the general conditions necessary for the appearance of chelation are well understood[1],[2]; the general case of a substance which in solution in an appropriate solvent forms but a single polymer, the dimer say, can be quantitatively described in terms of the equilibrium constant corresponding to polymerization[1]; the contribution of hydrogen bonding to crystal structure is discussed in detail in books devoted to this subject[3] or to the general subject of chemical bonding[2].

Liquid systems containing substances which form as the result of hydrogen bonding a large number of chainlike and ringlike polymers, e.g., the alcohols, are in principle amenable to the mathematical description derived by E. Lassettre[4] or to that derived by J. Kreuzer[5]. The description afforded by the former, despite its elegant simplicity and its successful use in the review article

by this same author[1], is limited conceptually by the arbitrary nature of the two parameters in terms of which physical quantities of interest are expressed. That afforded by the latter author appears more closely related to the physical situation and is therefore utilized where necessary in the discussion which follows.

Whatever the applicability and the serviceability of the chosen mathematical formalism the complexity of alcoholic solutions greatly complicates the experimental methods used in studying them and obscures the physical significance of measurements made with such solutions. The observations of W. Jones[6] on the viscosity of alcohol-carbon tetrachloride solutions are, however, readily understood. As was noted by Jones none of the standard expressions for the viscosity of liquid systems predicts the observed minima in the viscosity-composition diagrams for ethyl alcohol, for n-propyl alcohol, and for n-butyl alcohol in carbon tetrachloride. A simple treatment which takes into account the molecular complexity of such solutions does so*.

Solutions of such complexity are most easily studied by means of the strong spectroscopic absorption maxima characteristic of the hydroxyl group. The

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* See Appendix.

appearance of these maxima and their relation to the nearby band structure attributed to hydroxyl groups involved in hydrogen bonding have been studied extensively for many compounds containing hydroxyl groups. As a result of such investigations it is usually assumed that the absorption by hydroxyl groups involved in hydrogen bonding either through the oxygen atom or through the hydrogen atom of the hydroxyl group is shifted away from the absorption maxima characteristic of the unbonded hydroxyl group. One then has by the Beer-Lambert law of optical absorption that

$$T = e^{-\epsilon_\infty c_1 l} \qquad (1a)$$

$$T = e^{-\epsilon_\infty \alpha c l} \qquad (1b)$$

where T = the optical transmission of a given solution.

ϵ_∞ = the molar absorption coefficient of alcohol at infinite dilution in the solvent being used.

l = the optical path length.

c_1 = the molar concentration of monomeric alcohol.

c = the molar concentration of total alcohol.

α = the fraction of alcohol in the form of monomer.

Hence one can obtain from optical transmission measurements a knowledge of α as a function of the concentration of alcohol in the solution. From this knowledge in turn one can obtain further information relating to these solutions. The difficulty of such a task is greatly reduced by

restricting oneself to nonpolar solvents with which the alcohol in question does not react to form solvent-solute complexes. Several alcohols have been studied and treated in just such a manner: ethyl alcohol by J. Errera[7], phenol by O. Wulf[8], benzyl alcohol by J. J. Fox[9], and the lower aliphatic alcohols and phenol by R. Mecke and associates[10],[11],[12],[13],[14]. Usually the solvent used is either carbon tetrachloride or benzene for the reason noted above.

Since the interpretation of the information obtained is ultimately no better than the assumption previously noted regarding the optical absorption of the hydroxyl group, it would be well at this point to examine the experimental check on this point afforded by the vapor pressure measurements of A. Niini[15] for the system CH_3OH-CCl_4. Other vapor pressure measurements for alcohol-carbon tetrachloride systems, such as those of G. Scatchard on CH_3OH-CCl_4[16], or those of F. Ishikawa on C_2H_5OH-CCl_4[17], do not include measurements for extremely dilute solutions of alcohol as do those of Niini, and are for that reason unsuitable since it is exactly these very dilute solutions that are of greatest interest. Unfortunately one is also restricted to the single case of CH_3OH-CCl_4 since Niini's own data for the system C_2H_5OH-CCl_4 are not sufficiently self-consistent in the region

of interest to be of value.

As Niini has shown it is possible to calculate the partial vapor pressures of the individual components of a binary system such as CH_3OH-CCl_4 from an accurate knowledge of the total vapor pressure of the system as a function of the composition of the liquid phase. From this knowledge in turn one can determine the concentration of monomeric alcohol in the liquid phase as a function of the composition of the latter. Consider an arbitrary, dilute solution of alcohol in carbon tetrachloride. It is assumed, first, that the vapor phase in equilibrium with the above solution is ideal, second, that the vapor phase consists of monomeric alcohol and carbon tetrachloride, and third, that the monomer obeys Henry's law. The liquid phase will consist of n_0 moles of carbon tetrachloride, n_1 moles of monomeric alcohol, n_2 moles of dimeric alcohol, and so on for polymeric alcohol of all orders. The true mole fraction of monomer is given by the expression

$$x_1 = \frac{n_1}{(n_0 + \sum_{p=1}^{\infty} n_p)} \qquad (2)$$

Henry's law for the monomer takes the form

$$p_1 = kx_1 \qquad (3)$$

where p_1 = the partial vapor pressure of alcohol.

k = Henry's law constant for the monomer.

x_1 = the mole fraction of monomer in the liquid phase.

Equation (3) can also be expressed in the form

$$p_1 = k\gamma x_a \qquad (4)$$

where γ = the activity coefficient of alcohol in the liquid phase, defined with respect to infinite dilution in carbon tetrachloride.

x_a = the apparent or formal mole fraction of alcohol in the liquid phase.

The apparent mole fraction x_a is that which one would determine by chemical analysis. Mathematically x_a can be related to the mole fractions of the various polymers by the relation given below.

$$x_a = \frac{\sum_{p=1}^{\infty} pn_p}{(n_o + \sum_{p=1}^{\infty} pn_p)} \qquad (5)$$

The activity coefficient γ contained in equation (4) can be cast into a new form by equating equations (3) and (4) and utilizing the expressions for x_1 and x_a given above.

$$\gamma = \frac{n_1(n_o + \sum_{p=1}^{\infty} pn_p)}{(n_o + \sum_{p=1}^{\infty} n_p)(\sum_{p=1}^{\infty} pn_p)} \qquad (6)$$

Since α, the fraction of alcohol which exists as monomer in the solution being considered, is given by

$$\alpha = \frac{n_1}{(\sum_{p=1}^{\infty} pn_p)} \qquad (7)$$

equation (6) can itself be re-expressed in the form

$$\gamma = \frac{\alpha(n_o + \sum_{p=1}^{\infty} pn_p)}{(n_o + \sum_{p=1}^{\infty} n_p)} \qquad (8)$$

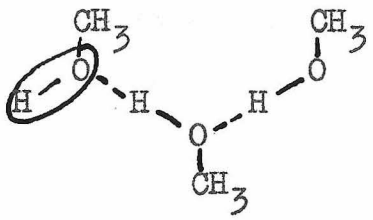
For dilute solutions the ratio of the bracketed terms is very nearly equal to one so that for such solutions $\gamma = \alpha$.

The vapor pressure data of A. Niini[15] for the system CH_3OH-CCl_4 have been used to calculate both k and γ, the former by extrapolation of the quantity p_1/x_a to infinite dilution of CH_3OH in CCl_4, and the latter by direct substitution of calculated values of p_1 and known values of x_a into equation (4) once k had been determined.

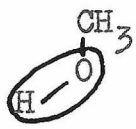
A comparison of γ from vapor pressure data and α from spectroscopic data has been made in figure (1). Superficially the agreement is striking. It is well, however, to emphasize that both sets of measurements involve extrapolations to infinite dilution, the vapor pressure data for the Henry's law constant for methyl alcohol in carbon tetrachloride, the optical absorption data for ϵ_∞, the molar absorption coefficient for methyl alcohol at infinite dilution in carbon tetrachloride, so that the excellent agreement may be in part fortuitous. Still, the error involved in these extrapolations appears from a consideration of the original data to be less than five percent.

In the event that the optical absorption of hydroxyl groups not directly involved in hydrogen bonding but adjacent to hydroxyl groups which are involved in bonding cannot be distinguished from that of the monomer, the

error introduced into α will be roughly twice the experimental error mentioned. To paraphrase, the question is whether the hydroxyl group indicated in Case A absorbs at the same or essentially the same wavelength as does that indicated in Case B.



Case A



Case B

The evidence just examined and illustrated in figure (1) while not conclusive favors the contention that it does not, and in addition suggests that for dilute solutions γ, the activity coefficient of methyl alcohol defined earlier, and α, the fraction of alcohol in the form of monomer, are equivalent within the limits of experimental error.

The remainder of the data on the alcohols studied by R. Mecke and associates yields one further feature of interest. As shown in figure (2), α for the alcohols indicated falls along a single curve, for any given alcohol the variation of α from the mean curve being no greater than the estimated experimental error. In the light of the preceding comparison it appears that the activity coefficients of these alcohols in the liquid phase are

very nearly the same for equal molar concentrations of alcohol. The variation of this single, average quantity for a temperature of about 20 C. is shown in figure (3). This variation with the composition of the liquid phase can be approximately represented by the expression

$$\alpha = (1/kx_a)(1 - e^{-kx_a}) \qquad (9)$$

where k is about 60.

As one progresses up the homologous series of n-aliphatic alcohols one would expect a decrease in the extent of hydrogen bonding polymerization. The effect for the first few members of the series is apparently slight. Even the change from aliphatic alcohol to phenol resulted in but a small, possibly non-existent, effect.

The cryoscopic measurements of F. Getman[18] on solutions of various alcohols in dioxane and in benzene, and the isopiestic measurements of E. Lassettre and R. Dickinson[19] on the system phenol-benzene indicate that the above regularities and simple relations will be confined to a restricted class of solvents. The observations of Getman indicated an association of solvent and solute in dilute solutions of alcohols in dioxane and in benzene. The data of Lassettre and Dickinson have been converted from f to α by means of the following relation derived by J. Kreuzer[5]:

$$-\ln \alpha = \frac{f - 1}{f} + \int_0^c \frac{f - 1}{f\, c}\, dc \qquad (10)$$

where α = the fraction of alcohol in the form of monomer.

f = the mean polymerization number, $\bar{M}/M$, of phenol in benzene.

$\bar{M}$ = the average molecular weight of phenol in benzene.

M = the formula weight of phenol.

The conversion from f to α was made in order to compare α for phenol in benzene with α measured optically for phenol in carbon tetrachloride. The upper curve in figure (4) is that for phenol in benzene, the lower curve a composite of the absorption data of R. Mecke[10], E. Hoffman[12], and O. Wulf[8] for phenol in carbon tetrachloride. The variation of α with concentration for phenol in benzene is consistent with an equilibrium between monomeric phenol and dimeric phenol, the dimer constant associated with the equilibrium

$$2\ PhOH \rightarrow (PhOH)_2 \qquad K = \frac{(PhOH)_2}{(PhOH)^2}$$

being about 0.5. Phenol in carbon tetrachloride, however, apparently forms polymers of many orders. It does not seem reasonable that phenol should form polymers of many orders in one non-polar solvent and but a single polymer, the dimer, in another non-polar solvent. The possibility of association of phenol with benzene[20] suggests that the simple dimeric association noted above may be merely

apparent rather than real.

Restricted as one may be to solvents not containing oxygen, etc., and without multiple bonds, that is, to solvents such as carbon tetrachloride and hexane, the variation of α with the concentration of alcohol in carbon tetrachloride and with temperature can be made to yield a great deal of information over and above that already noted. R. Mecke, on the assumption* that the equilibrium constant for the reaction

$$(ROH)_{g-1} + ROH \rightarrow (ROH)_g$$

$$k_{g-1,g} = \frac{(ROH)_g}{(ROH)_{g-1}(ROH)} \qquad (11)$$

is independent of g, has derived a number of useful relations, recently summarized in a review[21], as consequences of the above assumption and of the mathematical formalism developed by J. Kreuzer[5] and extended by R. Mecke[22]. In particular, it is found that the following relation should be true, as it appears to be for not too dilute solutions of alcohol in carbon tetrachloride.

$$\epsilon \cdot c = K\epsilon_\infty - (K\sqrt{\epsilon_\infty})\sqrt{\epsilon} \qquad (12)$$

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* The same assumption treated in a different manner led O. Redlich to the surprising result that the constant defined above for a given alcohol should also be independent of the particular non-polar solvent used--barring solute-solvent association (24). However, the mathematical formalism used in arriving at this result is complex and its relation to the physical situation not at all clear.

where ϵ = the apparent molar absorption coefficient of the alcohol in question.

$\epsilon = (-\ln T)/cl$

ϵ_∞ = the molar absorption coefficient at infinite dilution.

c = the formal concentration of alcohol.

K = a constant.

In very dilute solutions, however, the behaviour of ϵ is such that Mecke concludes that there is little or no dimeric association, hence that association begins with a trimer for which Mecke on the basis of dielectric measurements[23],[24] suggests a cyclic structure. The observed behaviour of ϵ at low concentrations of alcohol need not be due to the absence of dimeric association but to non-conformity of the various equilibrium constants, especially those for small g, with the initial assumed condition. The experimental work which follows is primarily an attempt to distinguish between the two possibilities by studying the variation of T, hence α, with the concentration of alcohol for very dilute solutions of methyl alcohol and of ethyl alcohol in carbon tetrachloride.

II. Experimental:

Optical transmission measurements for dilute solutions of ethyl alcohol and of methyl alcohol in carbon tetrachloride were obtained using a Beckman Spectrophotometer at wavelengths corresponding to the strong absorption maximum in the vicinity of 0.96 microns. Measurements were carried out using 10 cm. glass cells with silica windows, one cell containing the solution of interest and the other pure solvent of the same degree of dryness as that used in preparing the solution. Temperature ranged from 21°C. to 23°C.

Primary measurements on which calculations were based were made with an optical slit width corresponding to 35 cm^{-1}. There was no detectable difference between measurements for this slit width and similar measurements for a slit width corresponding to 25 cm^{-1}. However, transmission measurements for a slit width corresponding to 45 cm^{-1} were slightly larger than the primary measurements mentioned above, the difference varying from 0% for 100% transmission to 1% for 80% transmission.

The amount of stray light in the system was considered negligible for the following reasons: the transmission of an aqueous solution of $CuCl_2$ (2.3 g/liter) for a path length of 10 cm. was effectively zero in the spectral region of interest; the insertion of a gelatin

infrared filter into the optical path had no noticeable effect on transmission data.

Solutions of alcohol in carbon tetrachloride were prepared using C.P. alcohols containing 0.3% to 0.4% of water by weight as determined with Karl Fischer reagent, and C.P. CCl_4 distilled from P_2O_5. CCl_4 so dried and solutions of alcohol in CCl_4 so dried were exposed as little as possible to atmospheric air and were used as soon as possible after drying of the solvent, in most cases within a few hours. In the absence of an accurate analytical method for minute quantities of H_2O dissolved in CCl_4, solutions so handled were considered water free.

To determine the effect of a small quantity of H_2O on transmission measurements, data were obtained using CCl_4 previously saturated with H_2O, the transmission being measured relative to a blank containing CCl_4 also saturated with respect to H_2O. There was no apparent difference between these data and those obtained using dry solvent.

A brief study of the solubilization of water by alcohol was made in order to estimate possible effects on transmission and vapor pressure data of the presence of small quantities of water. A given amount of 99.7% ethyl alcohol was dissolved in dry CCl_4 and the solution titrated to turbidity with a dilute solution of water in alcohol. The compositions of the solutions so obtained

are given below and also graphically presented in figure (5).

The total vapor pressure of several dilute solutions of ethyl alcohol in carbon tetrachloride was determined using the apparatus schematically shown in figure (6). The solution of interest was introduced into vessel A through sidearm B which was then sealed. Dissolved air was removed by freezing the solution at about -70°C. and evacuating the vessel through sidearm C, then closing stopcock D, thawing the solution, refreezing and evacuating, etc. Three such cycles were sufficient to obtain a constant pressure reading on the mercury manometer after the solution had been permitted to come to thermal equilibrium with the water bath, the temperature of which was maintained within 0.03°C. of 25°C. as read on an uncalibrated thermometer. The height of the mercury column was read from a metric scale attached to the rear of the apparatus. The composition of a test solution was checked before and after the actual vapor pressure determination by means of the index of refraction of the solution as determined with an Abbé refractometer.

The formation of a white to gray scum on the surface of the right hand mercury meniscus made reading its height difficult and was an important factor in limiting reproducibility to 0.3 mm. of mercury. Since the above effect was observed both for solutions of alcohol in carbon

tetrachloride and for carbon tetrachloride alone it was presumably due to the presence of impurities, possibly chloroform, in the solvent used.

Inasmuch as the presence of slight amounts of water could seriously affect the accuracy of the measurements made on the more dilute solutions, experimental runs were made first with CCl_4 dried as described above and then with added P_2O_5 in vessel A. The presence of P_2O_5 lowered the vapor pressure by as much as 1 mm. of mercury. Probably for this reason the vapor pressures obtained for solutions containing less than about 0.0025 mole fraction of alcohol were erratic and unreliable.

Transmission data for methyl alcohol in dry carbon tetrachloride at a wavelength of 960 millimicrons.

$\frac{\text{grams of alcohol}}{\text{liter of } CCl_4}$	Transmission
0.00	1.000
0.11	0.996
0.26	0.988
0.33	0.986
0.50	0.979
0.63	0.975
0.82	0.966
1.10	0.955
1.18	0.952
1.67	0.936
1.98	0.927
2.37	0.916
3.92	0.884

Transmission data for ethyl alcohol in dry carbon tetrachloride at a wavelength of 962 millimicrons.

$\frac{\text{grams of alcohol}}{\text{liter of } CCl_4}$	Transmission
0.00	1.000
0.24	0.993
0.36	0.988
0.56	0.983
0.74	0.978
1.12	0.968
1.30	0.965
1.54	0.959
1.64	0.958
1.90	0.951
2.28	0.943
2.48	0.936
3.00	0.929
3.18	0.926

Data for the solubilization of water by ethyl alcohol.

% H_2O by weight	% C_2H_5OH by weight
0.010	0.00
0.016	0.13
0.011	0.16
0.018	0.33
0.032	0.38
0.024	0.42
0.038	0.46
0.048	0.86
0.067	1.26
0.082	1.60

Vapor Pressure data for the system C_2H_5OH-CCl_4.

Mole fraction of alcohol	p(mm. Hg)
0.00000	114.9
0.00227	119.2
0.00440	123.5
0.00540	125.7
0.00654	127.7
0.00781	129.8
0.00919	131.2

III. Discussion:

The transmission data for methyl alcohol and for ethyl alcohol in carbon tetrachloride were fitted by least squares to a curve of the form

$$-\ln T = a_0 + a_1 c + a_2 c^2 + a_3 c^3 + a_4 c^4 \qquad (13)$$

where c is the concentration of alcohol in grams per liter of carbon tetrachloride. The coefficients determined in this manner are given below:

ethyl alcohol	methyl alcohol
$a_0 = -0.00047989$	$a_0 = -0.0000671927$
$a_1 = +0.03835698$	$a_1 = +0.04239897$
$a_2 = -0.01441904$	$a_2 = +0.001335789$
$a_3 = +0.00626413$	$a_3 = -0.00227573$
$a_4 = -0.00098266$	$a_4 = +0.00031224$

The magnitude of the constant term a_0, which in principle should be zero, is a rough measure of the inaccuracy of the fit obtained. Originally the intention had been to relate the coefficients a_1 and a_2 to the molar absorption coefficient and to the dimer constant for the above alcohols. It was found, however, that these coefficients were extremely sensitive to the number of terms included in expressions analagous to equation (13) so that any theoretical significance attached to these coefficients also varied with the number of terms included. As a result the curves in figures (9) and (10) are based on a

visual estimate of the slope of the curves in figures (7) and (8) as a function of the concentration of alcohol.

The relations used to obtain the two quantities of immediate concern, ϵ_∞, the molar absorption coefficient at infinite dilution, and k_{12}, the dimer constant defined by

$$k_{12} = \frac{(ROH)_2}{(ROH)^2} \qquad (14)$$

are consequences of the Beer-Lambert law and the relation

$$\frac{1}{\alpha} = \sum_{n=1}^{\infty} n k_{1n} c_1^{n-1} \qquad (15)$$

derived by Kreuzer.

From equation (1b)

$$-\ln T = \epsilon_\infty \alpha c l \qquad (16)$$

$$\epsilon_\infty = \lim_{c \to 0} \frac{-\ln T}{\alpha c l} \qquad (17)$$

Although ϵ_∞ can then be obtained from a plot of $(-\ln T)/cl$ versus c as the intercept at c=0, the extreme sensitivity of $(-\ln T)/cl$ to small errors in T made the necessary extrapolation to zero concentration quite difficult. The alternate method of obtaining ϵ_∞ outlined below was found to be more satisfactory.

Differentiation of equation (16) with respect to c and passage to the limit of infinite dilution yields the relation

$$\lim_{c \to 0} \frac{d(-\ln T)}{dc} = \epsilon_\infty l \qquad (18)$$

whence one sees that ϵ_∞ is proportional to the slope at c=0 of curves such as those in figures (7) and (8). Proceeding in this manner one finds that for methyl alcohol $\epsilon_\infty = 0.13_6$ liter mole^{-1} cm^{-1} and that for ethyl alcohol $\epsilon_\infty = 0.15_3$ liter mole^{-1} cm^{-1}.

It can also be shown that the second derivative of -ln T with respect to c can be put in the useful form

$$\lim_{c\to 0} \frac{d^2(-\ln T)}{dc^2} = 2\epsilon_\infty l \lim_{c\to 0} \frac{d\alpha}{dc}$$

$$" \qquad = -4\epsilon_\infty l k_{12} \qquad (19)$$

where the second form of equation (19) is a consequence of equation (15). Figures (9) and (10) in conjunction with equation (19) were used to determine the dimer constants for methyl alcohol and for ethyl alcohol in carbon tetrachloride. In both cases k_{12} is approximately 1 liter mole^{-1} as compared with the constant $k_{g-1,g}$ defined earlier which was found by Mecke to be about 3 for large g. Accordingly it would appear that $k_{g-1,g}$ is a function of g, albeit a slowly varying one, which approaches 3 for large g.

As was previously mentioned the assumption that $k_{g-1,g}$ is independent of g leads to a tidy and simple mathematical formalism for the description of some of the physical properties of solutions of alcohols in a non-polar solvent such as carbon tetrachloride. While such a

simplification is useful the value of k_{12} above suggests that $k_{g-1,g}$ is not independent of g. As alternative procedures one might assume that $\Delta H_{g-1,g}$ or that $\Delta S_{g-1,g}$ is independent of g. With respect to the first assumption one should note that the broadness of the absorption band attributed to polymers is sometimes taken as indicating the existence of hydrogen bonds of slightly different kinds and strengths, presumably as many kinds as there are different orders of polymers. The assumption that $\Delta H_{g-1,g}$ is independent of g while incompatible with this interpretation is consistent with the suggestion of Badger and Bauer[26] that the observed width of the association band could arise from the interaction of low frequency intermolecular vibrations with the hydroxyl vibration. Despite the meagreness of support for the above assumption one might profitably examine its consequences. The two quantities $\Delta H_{g-1,g}$ and $\Delta F_{g-1,g}$ have been indirectly determined by Mecke in moderately concentrated solutions of alcohol in carbon tetrachloride, hence for large g. At room temperature

$$\Delta F_{g-1,g} = -596 \text{ cal.}$$
$$\Delta H_{g-1,g} = -4720 \text{ cal.}$$

so that

$$\Delta S_{g-1,g} = -14.0 \text{ cal. deg}^{-1}$$

Now using the value for k_{12} obtained above one finds that

$$\Delta F_{12} = 0 \text{ cal.}$$

$$\Delta H_{12} = -4720 \text{ cal. (assumed)}$$

so that

$$\Delta S_{12} = -16.5 \text{ cal. deg.}^{-1}$$

One immediately notes the large, possibly unreasonable decrease in ΔS_{12} compared to $\Delta S_{g-1,g}$.

Consider the analagous calculations in the light of the assumption that $\Delta S_{g-1,g}$ is independent of g.

$$\Delta F_{12} = 0 \text{ cal.}$$

$$\Delta S_{12} = -14.0 \text{ cal. deg.}^{-1} \text{ (assumed)}$$

so that for this case

$$\Delta H_{12} = -4100 \text{ cal.}$$

compared to $\Delta H_{g-1,g} = -4720$ cal. There is very little reason to prefer either of the above assumptions although the latter is not open to the criticism noted with respect to the former, and leads to a result compatible with the notion that hydrogen bond strength increases with increasing degree of polymerization[2].

In principle one should be able to utilize the recent measurements of K. Pitzer[27] on the heat capacity of methanol vapor to differentiate between the two possibilities. Briefly, Pitzer attributed deviations of methanol vapor from ideality to the formation of polymers. On this basis he derived from his measurements the heat and the entropy of dimerization (in the vapor) and the heat

and the entropy changes corresponding to what he regards as the formation of a cyclic tetramer--or an appropriate mixture of trimer, tetramer, pentamer, etc. These quantities for a temperature of 350° K are given below:

$$\Delta H_{12} = -3220 \text{ cal.}$$
$$\Delta S_{12} = -16.5 \text{ cal. deg.}^{-1}$$
$$\Delta H_{14} = -24,200 \text{ cal.}$$
$$\Delta S_{14} = -81.3 \text{ cal. deg.}^{-1}$$

If the tetramer in question is indeed cyclic then the quantity $-\Delta S_{14}/4$ corresponding to the average decrease in entropy per bond, as well as the quantity $-\Delta H_{14}/4$ corresponding to the average enthalpy decrease per bond are much larger than the quantities $-\Delta S_{12}$ and $-\Delta H_{12}$, much larger than one would expect to be the case. Further, one might question the interpretation of a second order correction term to an equation of state as due to the formation of a specific polymer. There seems to be no doubt that dimeric alcohol exists in the vapor in a concentration sufficient to affect heat capacity measurements to a degree greater than that due to normal gas imperfections. The same cannot be said for higher polymers, the concentrations of which are so low that any effect due to their presence is quantitatively indistinguishable from the effects observable in their absence. The deviations from ideality observed by Pitzer were only about twice those that would

be observed for such substances as ether, acetone, etc. The greater part of this difference is apparently due to dimerization. The quantitative significance of the balance is uncertain.

The data given earlier in connection with the solubilization of water by alcohol represent an average solubilization of 0.11 moles of water per mole of alcohol for the concentration range studied. If one assumes that for very dilute solutions, such as those used in the above transmission measurements, the solubility of water, as distinguished from that portion in water-alcohol complexes, is constant and equal to that of water in pure carbon tetrachloride, then the solubilization noted represents the number of moles of water complexed with alcohol. Let the solubility of water in carbon tetrachloride be "a", then consider a given solution of alcohol in carbon tetrachloride which has been prepared using carbon tetrachloride saturated with respect to water. About 0.1a moles of water will be complexed with at most 0.2a moles of monomeric alcohol. The transmission of such a solution compared to a blank containing water saturated carbon tetrachloride will be increased by an amount corresponding to the decreased number of absorbing hydroxyl groups, namely about 0.4a. The solubility of water in carbon tetrachloride is about 0.01% by weight at room temperature, so

that for $T > 0.9$, corresponding to actual measurements, the error in T due to water-alcohol complexing is no more than about 0.001, or about the same as the observational error.

It is of course impossible to ascertain the nature of the water-alcohol complexes responsible for the observed solubilization but if one assumes that the reaction

$$ROH + H_2O \rightarrow ROH \cdot H_2O$$

is the primary one for dilute solutions, then one can calculate from the observed average solubilization the equilibrium constant for the above reaction. It is about 14 liter $mole^{-1}$.

The vapor pressure data obtained for dilute solutions of ethyl alcohol in carbon tetrachloride while of sufficient accuracy to obtain an approximate value for the Henry's law constant of ethyl alcohol in carbon tetrachloride were not sufficiently accurate to determine the small deviations from Henry's law due to association of the alcohol. The constant in question was found to be 2.09×10^3 mm. of mercury.

The formation of a gray scum on the mercury meniscus exposed to carbon tetrachloride vapors, and other considerations lead to the conclusion that the required accuracy, less than 0.1 mm. of mercury, can only be obtained with apparatus, technique, and care more detailed than that actually used. A study of such accuracy would be highly

desireable in order to confirm the observations made earlier on the relation between the activity coefficient of alcohol in the solution and the fraction of alcohol which exists as the monomer in the same solution.

IV. Conclusion:

The preceding considerations indicate several things. The vapor pressure measurements of A. Niini on the system CH_3OH-CCl_4 verify to some extent the usual assumption in optical absorption work that the strong, sharp absorption maxima characteristic of hydroxyl containing compounds is due to the hydroxyl group in the monomeric compound, e.g., monomeric alcohol, as distinguished from those in polymers. Moreover, it appears that the deviation of alcohols in solvents such as carbon tetrachloride from Henry's law is primarily due to hydrogen bonding polymerization and that the extent of this deviation for dilute solutions is the same for the lower aliphatic alcohols and phenol.

R. Mecke's assumption that $k_{g-1,g}$ for the reaction

$$(ROH)_{g-1} + ROH \rightarrow (ROH)_g$$

is independent of g, with the restriction that $k_{12}=0$, appears to be invalid for small g. In particular, the experimental evidence presented above indicates that k_{12} is about 1 liter mole^{-1}, hence implies that $k_{g-1,g}$ is in reality a slowly varying function of g. Possibly one might replace the assumption that $k_{g-1,g}$ is independent of g with either of the assumptions that $\Delta H_{g-1,g}$ or $\Delta S_{g-1,g}$ is independent of g. The latter is more consistent with current opinion but there is no strong reason to favor one

or the other and for most purposes the assumption that $k_{g-1,g}$ is independent of g is preferable to either of the others since it leads to the greatest simplification of the associated mathematics.

V. Figures:

Figure 1

A Comparison of α, the Fraction of Alcohol Which Exists as the Monomer, with γ, the Activity Coefficient of Alcohol in the Liquid Phase.

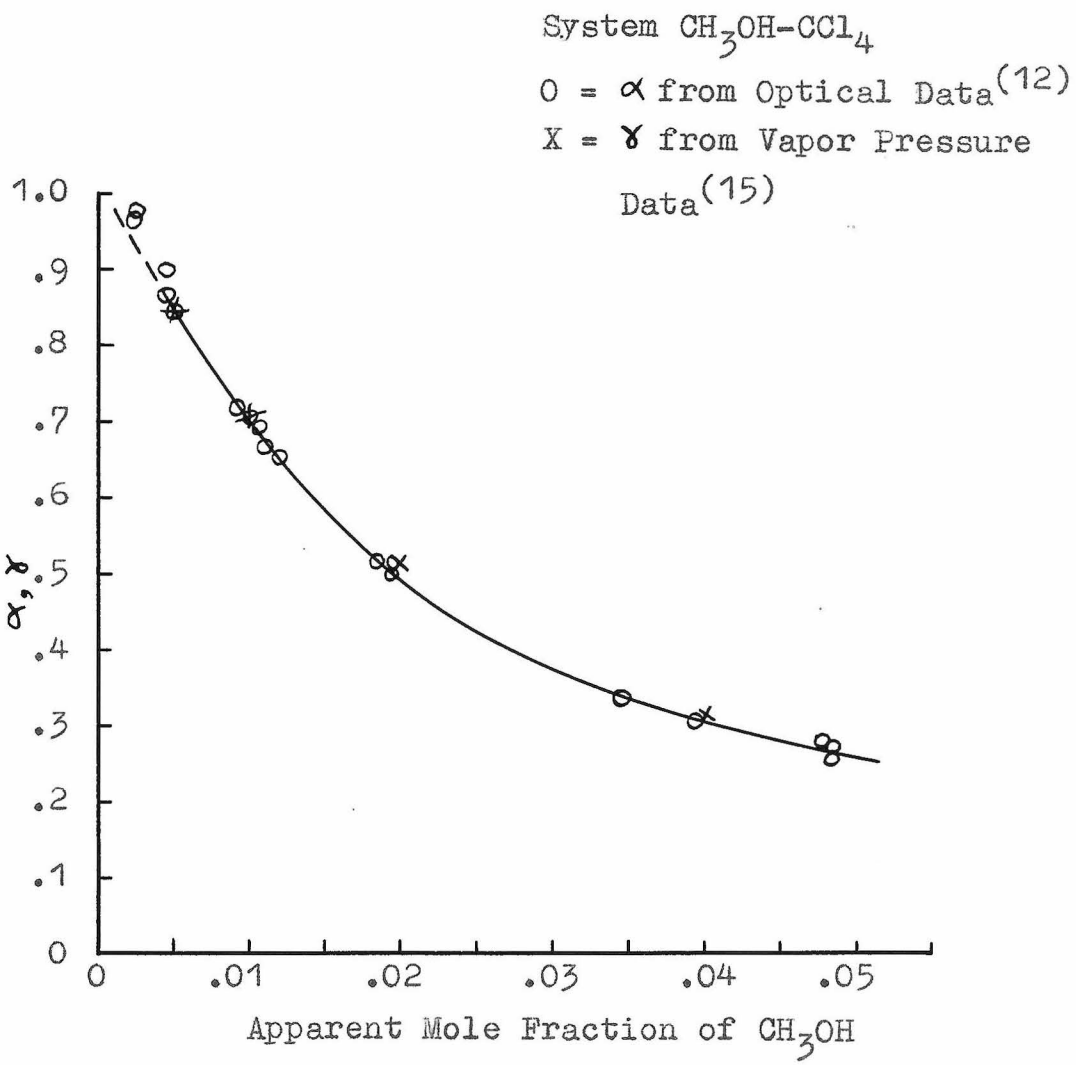


Figure 2

α, the Fraction of Alcohol Which Exists as the Monomer, for Various Alcohols as a Function of Their Respective Concentrations in Carbon Tetrachloride.

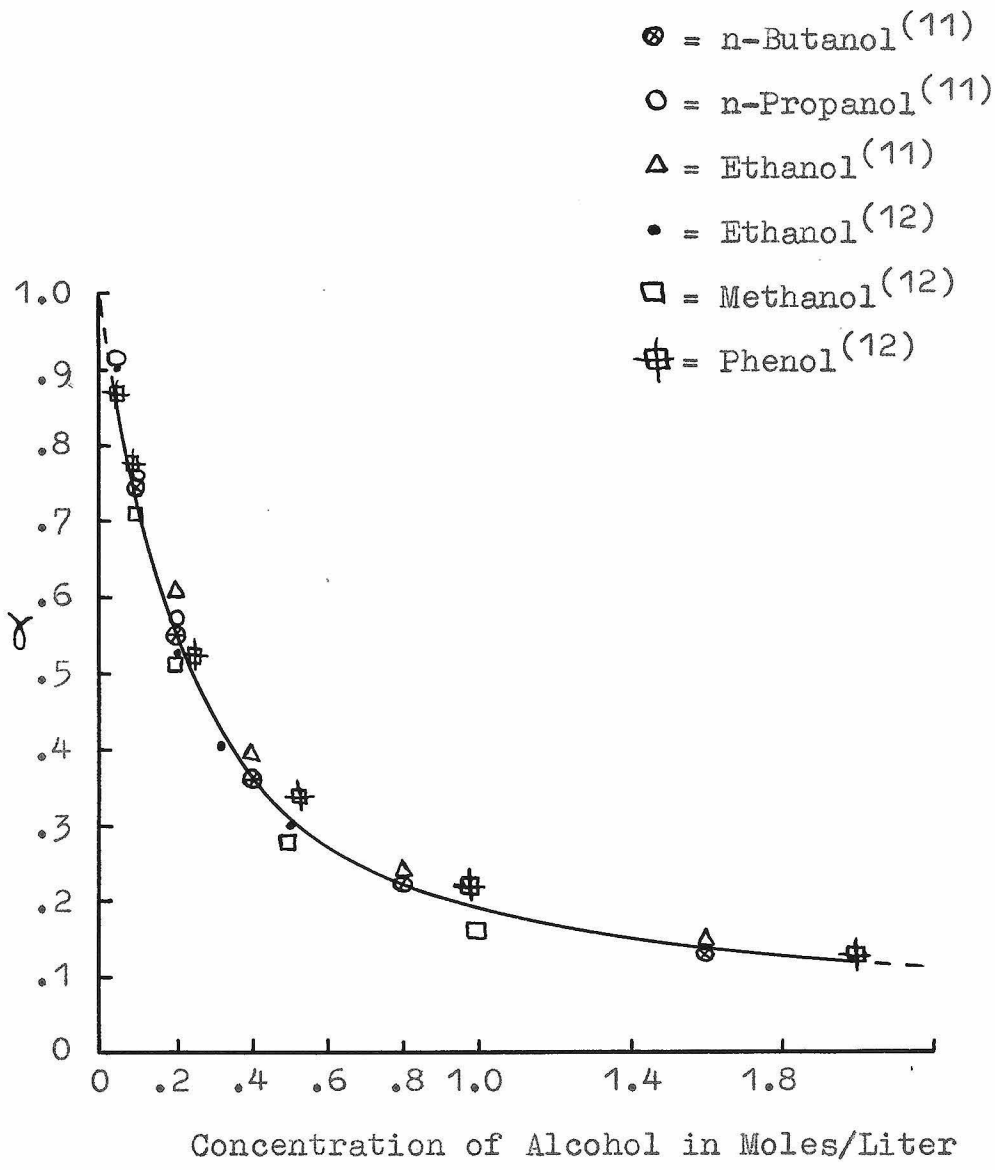


Figure 3

An Average Variation of α with Concentration for the Alcohols Noted in Figure (2).

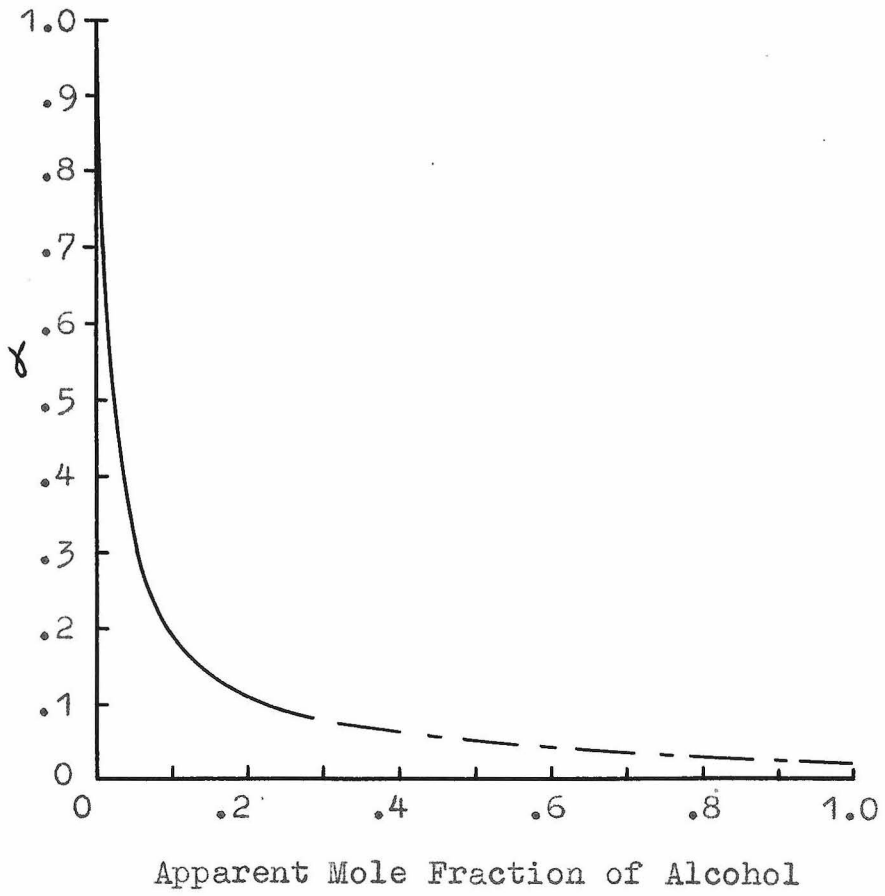


Figure 4

α for Phenol in the Solvents Benzene and Carbon Tetrachloride.

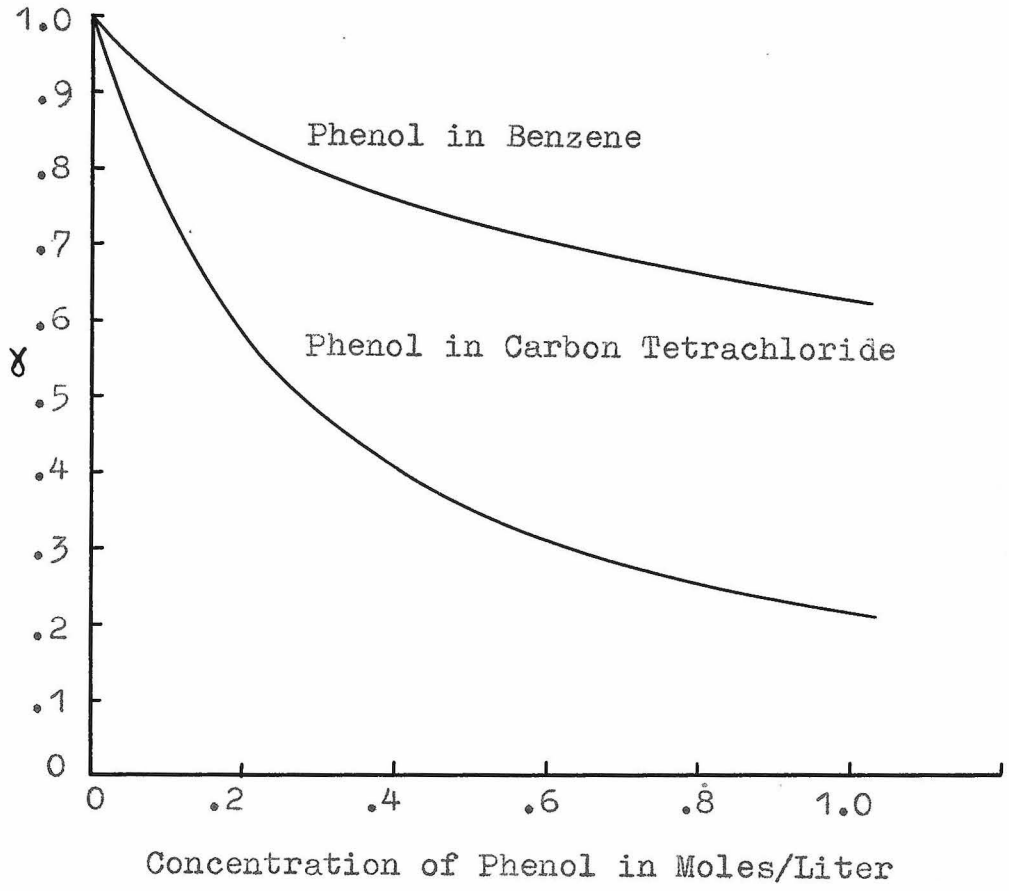


Figure 5

The Solubilization of Water by Ethyl Alcohol as Indicated by the Percentage Composition of Solutions of Ethyl Alcohol in Carbon Tetrachloride, the Solutions Being Saturated with Respect to Water.

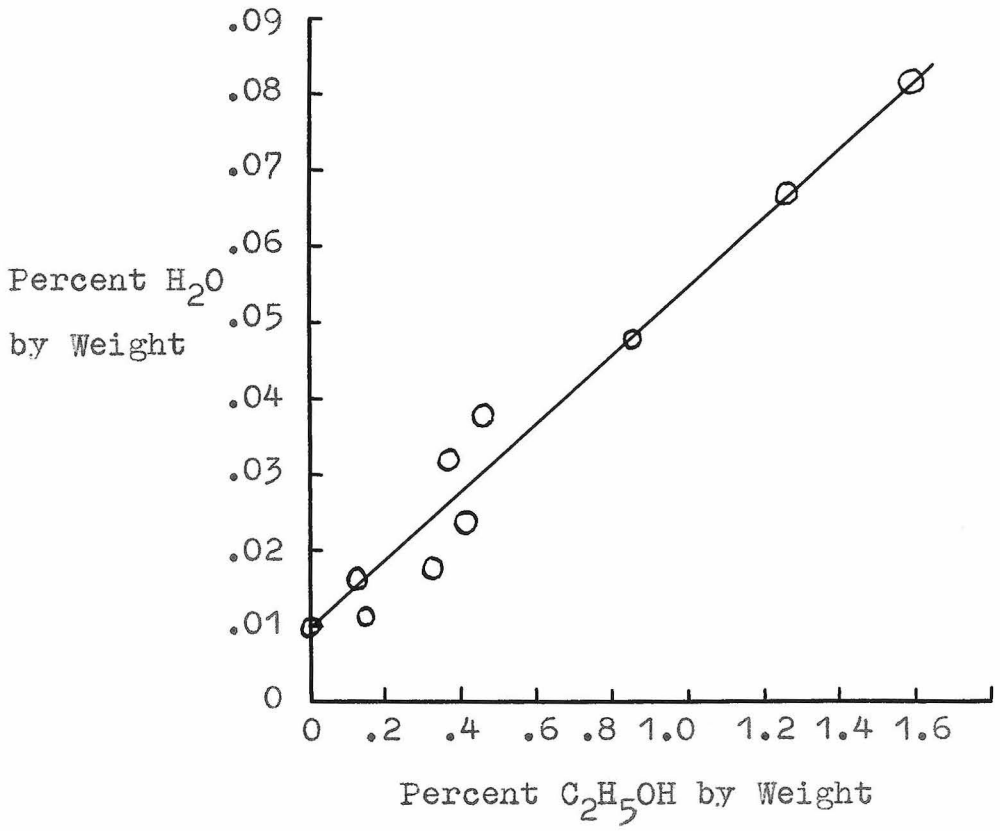
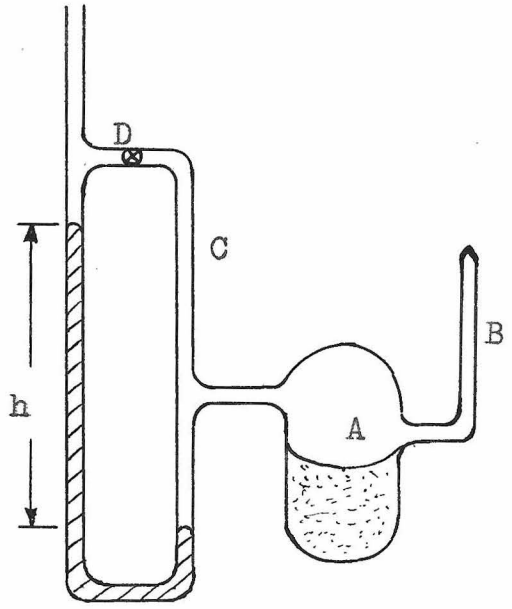


Figure 6

Manometer Used to Measure the Vapor Pressure of Solutions of Ethyl Alcohol in Carbon Tetrachloride.



Approximately one-quarter Scale

Figure 7

The Transmission of Solutions of Methyl Alcohol in Carbon Tetrachloride as a Function of the Concentration of Methyl Alcohol.

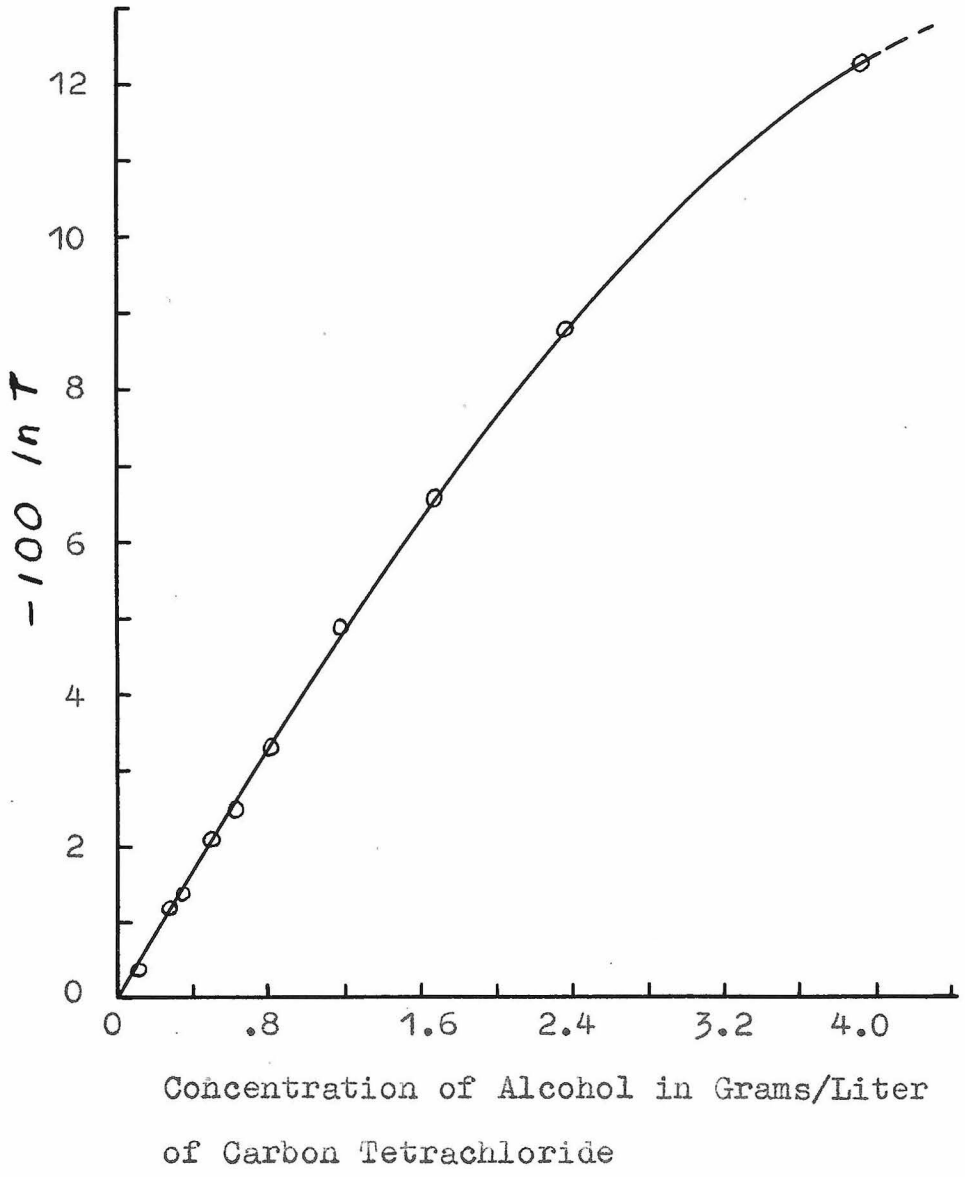


Figure 8

The Transmission of Solutions of Ethyl Alcohol in Carbon Tetrachloride as a Function of the Concentration of Ethyl Alcohol.

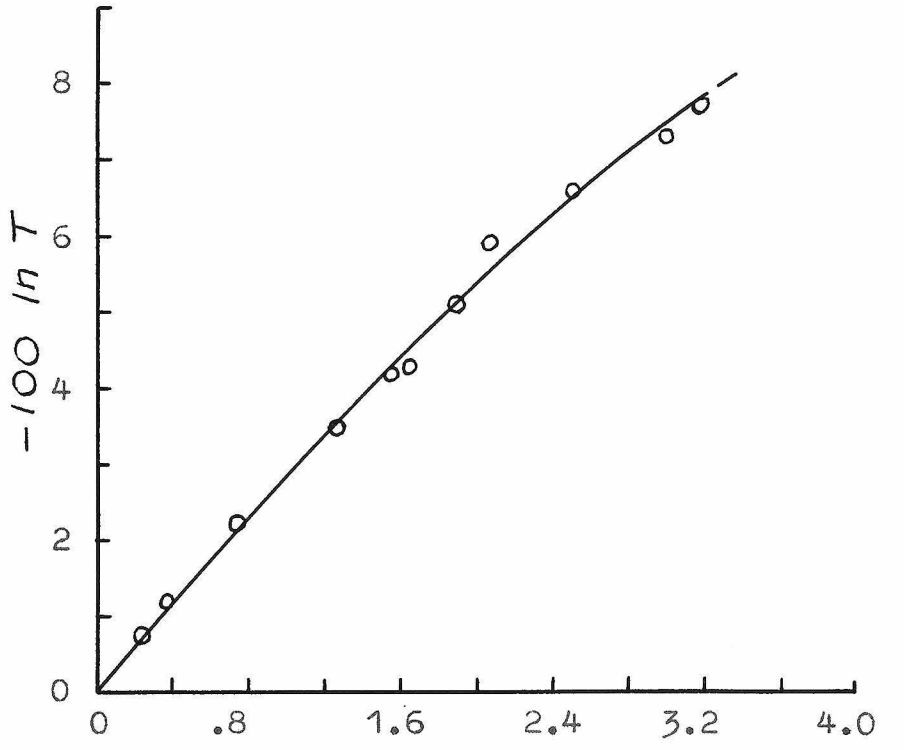


Figure 9

The Function (-d lnT)/dc for Methyl Alcohol in Carbon Tetrachloride.

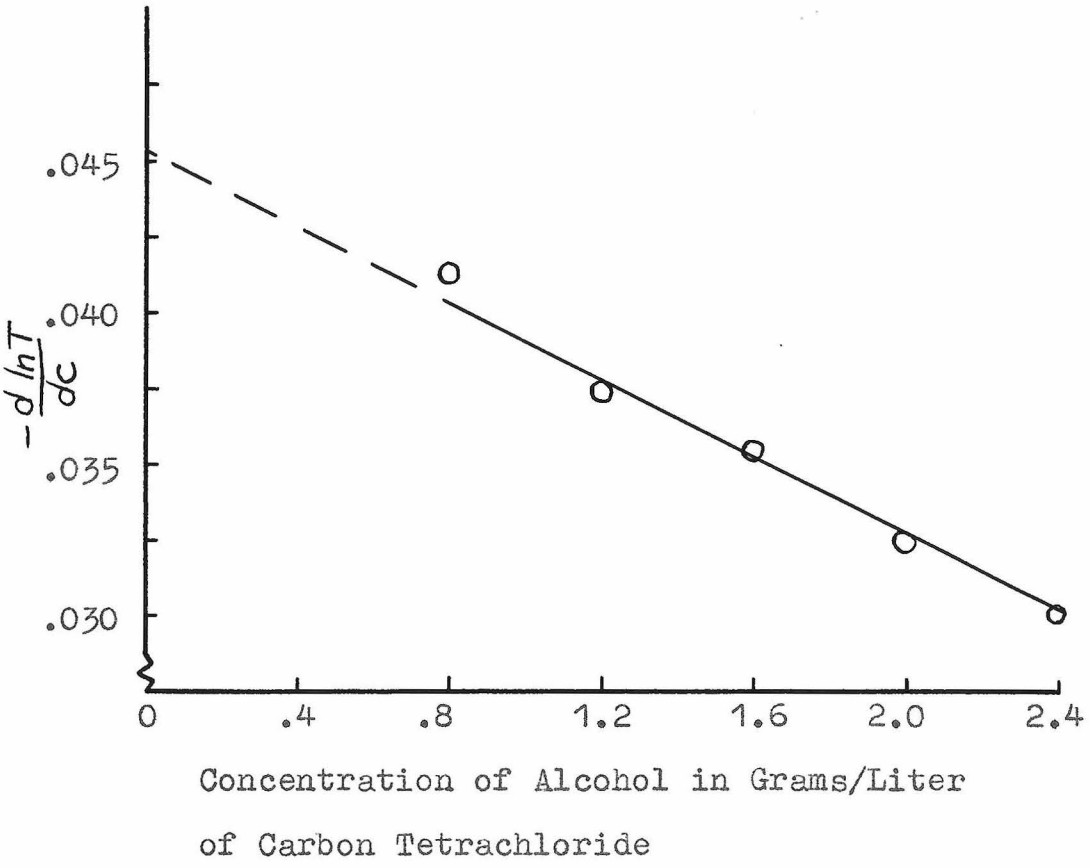
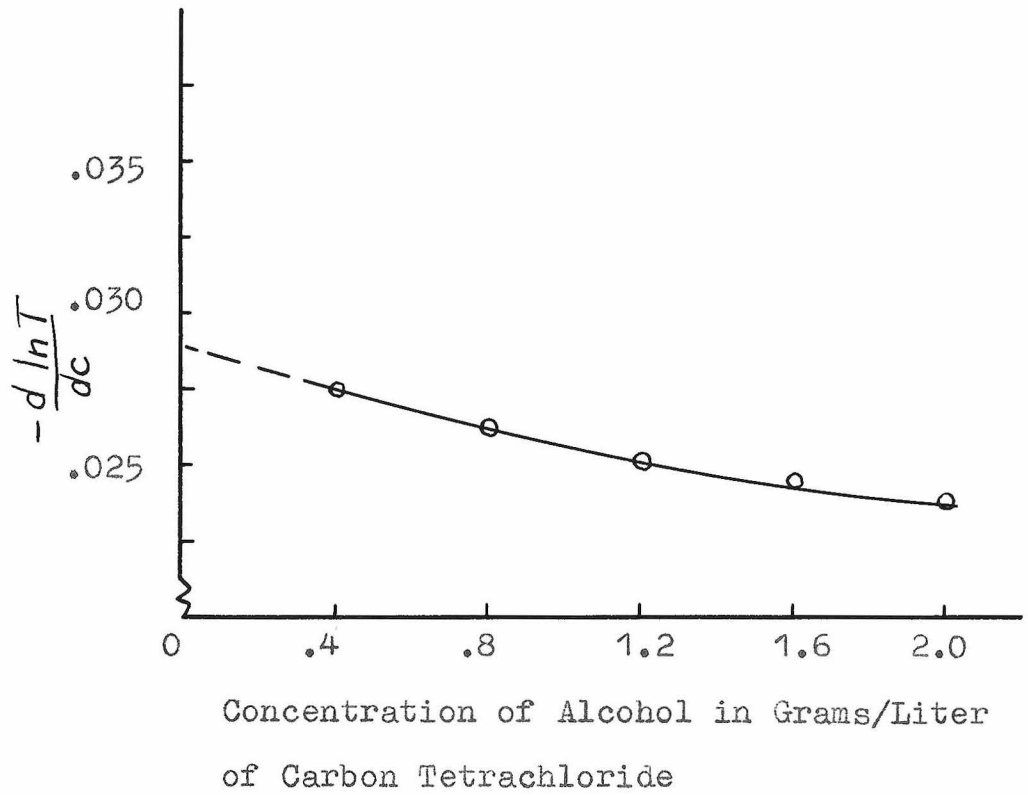


Figure 10

The Function (-d lnT)/dc for Ethyl Alcohol in Carbon Tetrachloride.



VI. Appendix: On the Viscosity of Alcohols in a Non-polar Solvent.

The equation

$$\phi = x_A\phi_A + x_B\phi_B \qquad (20)$$

has been employed[28] to relate the fluidity of a solution consisting of the two liquid components A and B with the fluidities, ϕ_A and ϕ_B, of the pure liquids and their mole fractions, x_A and x_B, in the solution. By analogy the fluidity of a dilute solution of an alcohol in a non-polar solvent such as carbon tetrachloride may be given by the equation

$$\phi = x_o\phi_o + A\sum_{n=1}^{\infty} c_n w_n \qquad (21)$$

where ϕ = the fluidity of the solution.

x_o = the mole fraction of the solvent.

ϕ_o = the fluidity of the pure solvent.

c_n = the concentration in moles per liter of the polymer formed as a result of the reaction $nROH \rightarrow (ROH)_n$.

w_n = "the inherent fluidity" of this polymer.

A = a constant relating concentration to mole fraction.

Although relation (20) is of limited validity[28],[29] even for mixtures of similar liquids and certainly cannot be expected to describe quantitatively the variation of viscosity of solutions with composition, it is a useful

approximation for dilute solutions which in the absence of hydrogen bonding of the lesser component would by assumption exhibit deviations from ideality much less pronounced than those actually observed.

Simple and interesting consequences of equation (21) can be derived if one assumes that

$$w_n = \frac{w_1}{n} \qquad (22)$$

that is, that the fluidity of polymer "n" varies inversely as the number of alcohol units which constitute the polymer. Since the concentration of polymer "n" can be expressed in the form

$$c_n = k_{1n} c_1^n \qquad (23)$$

equation (20) assumes the form

$$\phi = x_o \phi_o + A w_1 \sum_{n=1}^{\infty} \frac{k_{1n} c_1^n}{n} \qquad (24)$$

The function ϕ will have an extremum at that concentration for which

$$\frac{d\phi}{dc} = \phi_o \frac{dx}{dc}o + A w_1 \frac{dc}{dc}1 \sum_{n=1}^{\infty} k_{1n} c_1^{n-1} = 0 \qquad (25)$$

Now $c_1 = \alpha c$, so that

$$\frac{dc}{dc}1 = \alpha + c \frac{d\alpha}{dc} \qquad (26)$$

and

$$\frac{d\phi}{dc} = \phi_o \frac{dx}{dc}o + A w_1 (\alpha + c \frac{d\alpha}{dc}) \sum_{n=1}^{\infty} k_{1n} c_1^{n-1} = 0 \qquad (27)$$

$$\frac{d\phi}{dc} = -K\phi_o + A w_1 (\alpha + c \frac{d\alpha}{dc}) \frac{1}{\alpha} = 0 \qquad (28)$$

K and A are essentially the same conversion factor between concentration units and are numerically equal. Cancelling this factor one can put equation (28) in the final form

$$c = \frac{1 - f\frac{\phi_o}{w_1}}{\left|\frac{1}{\alpha}\frac{d\alpha}{dc}\right|} \qquad (29)$$

where $f = \bar{\alpha}/\alpha$, and can be shown to be equivalent to the mean polymerization number discussed earlier.

c = that concentration of alcohol at which there exists an extremum in ϕ, in this case a maximum.

In view of the equivalence between f and mean polymerization number f must be equal to or greater than one. Consequently, in order for a positive solution of equation (29) to exist the ratio ϕ_o/w_1 must be less than one. If w_1 for a given alcohol is of the same order of magnitude as the fluidity of its isomeric ether or of the chloro-substitute for the alcohol, then the ratio ϕ_o/w_1 is less than one for the lower aliphatic alcohols and the condition is satisfied. As one progresses up the homologous series of n-aliphatic alcohols the ratio ϕ_o/w_1 will of course increase until at some point in the series the condition that ϕ_o/w_1 be less than one will no longer be satisfied, and positive solutions to equation (29) will not exist.

Assuming the validity of relation (29) one can calculate the values of ϕ_o/w_1, or the values of w_1,

necessary to place the viscosity minima observed by W. Jones[6] at the observed concentrations of ethyl alcohol, of n-propyl alcohol, and of n-butyl alcohol in carbon tetrachloride. Equation (29) has been solved for ϕ_o/w_1 for these three cases. The appropriate values of $\left|\frac{1}{\alpha}\frac{d\alpha}{dc}\right|$ were obtained from figure (2), the appropriate values of f from the review article by R. Mecke[21]. The observed values of $c_{min.}$ from the paper by Jones are listed below as are the ratios of ϕ_o/w_1 computed in the manner described above.

alcohol	$c_{min.}(\frac{moles}{liter})$	ϕ_o/w_1
ethyl	1.50	0.11
n-propyl	0.517	0.19
n-butyl	0.169	0.41

The above values of ϕ_o/w_1 seem somewhat lower than one would intuitively expect but are not impossible.

The assumption on which the simple derivation above rests, namely that the fluidity of polymer "n" varies according to equation (27) is much too simple to be the basis of a quantitative description of a complicated physical situation. It was selected as being qualitatively representative of an inverse dependence of w_n on n.

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